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— Note —

FEM OBSERVATION OF WATER VAPOR ON TUNGSTEN

By

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The adsorption of water vapor on a clean tungsten surface is of interest not only as a fundamental problem in adsorption phenomena but also in the field of ultrahigh vacuum techniques. Up to the present, however, only a few studies of this system have been published¹⁻⁵). The field emission microscopy (FEM) provides an efficient means of following changes in the average work function and in the emission pattern with adsorption, desorption and decomposition of water vapor on a surface of tungsten tip. This note describes the FEM observation of the system, relating with available information on both the systems of hydrogen⁶) and oxygen⁷) on tungsten.

The clean surface of tungsten tip (Fig. 1) was exposed to water vapor at room temperature. The tip covered with water vapor was subjected to intermittent heat treatments at temperatures raised successively from room temperature to 2000°K without applied electric field. Each heat treatment was followed with simultaneous observations of the average work function and the emission pattern, the FEM cell being kept at 77°K throughout.

Five distinct stages were noted in the case of light dose (coverage $\theta \leq 1$): (1) During the initial adsorption of water vapor at room temperature, the average work function ϕ increased by 0.7 eV while the emission pattern seen in Fig. 2 could not be characterized by the adsorption of hydrogen⁶) or oxygen⁷). (2) Heat treatments of the tip at temperatures beginning from room temperature to 470°K caused distinct changes in pattern as shown in Fig. 3 and a further increase of ϕ by 0.3 eV ($\Delta\phi=1.0$ eV), along with a slight evolution of hydrogen. (3) Successive heat treatments at temperatures from 470°K to 860°K proceeded the desorption of hydrogen and caused a gradual decrease of ϕ by 0.6 eV ($\Delta\phi=0.4$ eV) and an appearance of the characteristic pattern of oxygen on tungsten as shown in Fig. 4. (4) During the heat treatments at temperatures from 860°K to 1500°K,

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the characteristics of the pattern remained unchanged and ϕ was kept almost constant, or $\Delta\phi=0.4$ eV. (5) The subsequent heat treatments at higher temperature up to 2000°K brought about reappearance of the clean tungsten pattern and the associated decrement of ϕ by 0.4 eV ($\Delta\phi\simeq 0$).

These observations are explained as follows. Admitting the dissociative adsorption of water molecules on tungsten at room temperature, *i. e.*

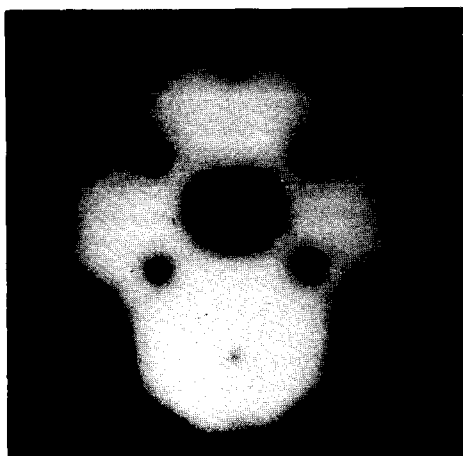
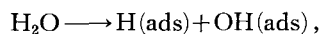


Fig. 1. Field emission pattern of clean tungsten tip

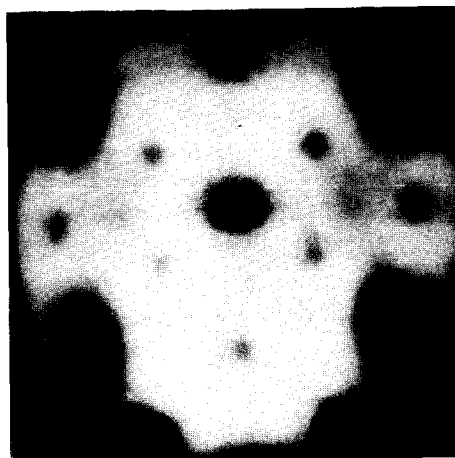


Fig. 2. H₂O-adsorption at room temperature, $\Delta\phi=0.7$ eV

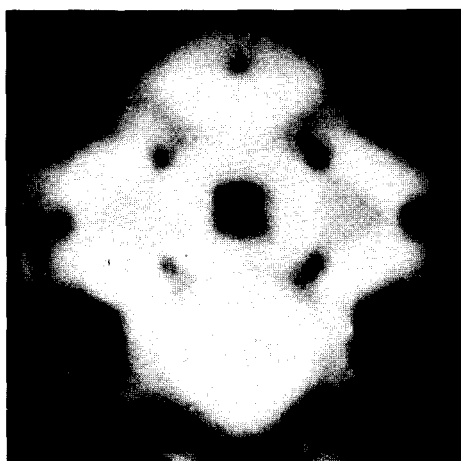


Fig. 3. After heat treatment at 470°K, $\Delta\phi=1.0$ eV

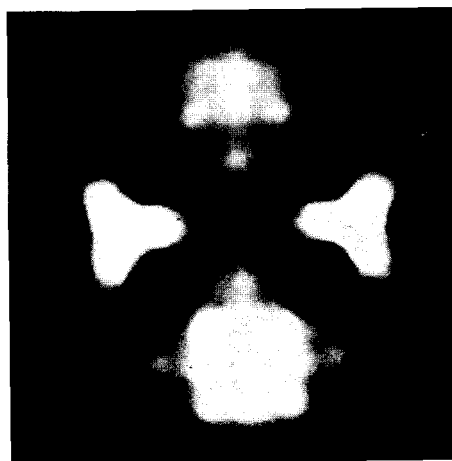
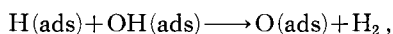


Fig. 4. After heat treatment at 860°K, $\Delta\phi=0.4$ eV

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we may attribute the considerable increase of ϕ in stage (1) to adsorbed hydrogen atoms, H(ads), and hydroxyl groups, OH(ads), both with negative dipole moment^{8,9}.

The OH(ads), at room temperature, is not likely to decompose⁴, but at elevated temperatures, as judged from the further increase of ϕ with the evolution of hydrogen in stage (2), it is likely that (a) it dissociates into H(ads) and O(ads) and (b) the H(ads) would react with OH(ads), *i.e.*



producing hydrogen molecules and O(ads), the latter contributing to the increase of ϕ . From both the decrease of ϕ in stage (3) and the appearance of characteristic patterns in stage (3) and (4), it is inferred that the desorption of H(ads) and the formation of tungsten oxides are taking place along with the dissociation of OH(ads) at temperature range of these two stages. The desorption of H(ads) at about 600°K is in harmony with the observation of hydrogen-tungsten system⁶ and the stable oxide pattern is identified with that of the oxygen-tungsten system at about 800°K or above⁷. In stage (5), at about 1500°K or above, tungsten oxides and oxygen are desorbed¹⁰ from the tip surface, with recovery of the clean surface.

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